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Dated 24 October 2003

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The Patent Office

Cardiff Road
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1. Your reference

PPD 70193/GB/P

2. Patent application number
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0228537.7

06 DEC 2002

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

SYNGENTA Limited
European Regional Centre
Priestley Road
Surrey Research Park, Guildford,
Surrey, GU2 7YH, United Kingdom

Patents ADP number *(if you know it)*

6254007002

0833 074 8001

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

4. Title of the invention

PARTICULATE SUSPENSIONS

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Michael James Ricks
Intellectual Property Department
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UNITED KINGDOM

Patents ADP number *(if you know it)*

0802 957 1001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
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See note (d))

YES (b)

Patents Form 1/77

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Continuation sheets of this form	37
Description	01
Claim(s)	01
Abstract	00
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Priority documents	
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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
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Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Syngenta Limited

Signature Joanna Chandler Date 5/12/02.

Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Joanna Carmen CHANDLER = 01344 414365

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PARTICULATE SUSPENSIONS

This invention relates to particulate suspensions and in particular to the use of reactive polymeric surfactants for the stabilisation of particulate suspensions.

In US 6262152 there is described a dispersion of solid particles which comprises (a) a liquid vehicle such as water or organic solvents; (b) particles that are at least substantially insoluble in the liquid vehicle; (c) a polymer dispersant having at least one segment soluble in the liquid vehicle and at least one segment insoluble in the liquid vehicle said insoluble segment having cross-linkable moieties; and (d) wherein the cross-linkable moieties on the insoluble segment of the polymer dispersant are cross-linked such that the insoluble segment of the polymer dispersant forms a cross-linked polymer with the particles entrapped therein. It is stressed that the particle is entrapped in a network formed by the insoluble polymer segment and the cross-linking bonds and that the cross-linking bonds are very stable and effectively prevent the particle from leaving the "core" formed by the polymer. Examples of suitable particles are stated to include pigments, insoluble dyes, metallic particles, biologically active compounds, pharmaceutically active compounds, polymer particles, hollow glass spheres etc. The Examples disclose pigments "encapsulated" within various a cross-linked polymers. In each case the dispersion contains 15% pigment and 10% polymer by weight prior to cross-linking. The only disclosure of the preferred ratio of polymer to pigment is that given in the Examples and it is clearly intended that the pigment particles are "entrapped" or "encapsulated" within the "core" of a substantial body of polymeric material as reflected by the ratio of pigment to polymer used in the examples. Such "entrapment" within the "network" or "matrix" around the particle is necessary to prevent it from leaving the "core" formed by the cross-linked polymer.

Despite the teaching of US 6262152 we have found that effective stabilisation of insoluble particles may be achieved using cross-linked polymers at greatly reduced concentrations as compared with those disclosed in US 6262152. Such reduced concentrations of polymer are particularly suitable for use with a dispersion of an agrochemical active ingredient within a medium in which it is substantially insoluble.

Thus according to the present invention there is provided a particulate suspension comprising a liquid phase having suspended therein a solid substantially insoluble in said liquid phase wherein the suspension is stabilised by the reaction product of

(i) a polymeric stabiliser having a hydrophilic moiety and a hydrophobic moiety and comprising a plurality of vinylic monomers, not being exclusively of vinylic esters or of their hydrolysed products, at least some of which contain functional groups capable of undergoing cross-linking nucleophilic or condensation reactions and

(ii) one or more substances contained in the liquid phase capable of undergoing a cross-linking reaction with said functional groups

wherein the ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended solid is less than 1 part of polymeric stabiliser per 5 parts of suspended solid.

The ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended solid is preferably from 1 part of polymeric stabiliser to 400 parts of suspended solid (1:400) to 1 part of polymeric stabiliser per 5 parts of suspended solid(1:5), for example from 1 part of polymeric stabiliser to 200 parts of suspended solid (1:200) to 1 part of polymeric stabiliser per 10 parts of suspended solid(1:10). An especially preferred range is from 1:10 to 1:100, for example from 1:20 to 1:75. A ratio of about 1:50 is especially preferred.

It is preferred that the suspended solid is an agrochemical active ingredient.

In view of the teaching of US 6262152 it is surprising that satisfactory particulate suspensions may be obtained using low levels of polymeric stabiliser according to the present invention. We have found that cross-linking of the polymeric stabiliser is still sufficient to "lock" it irreversibly to the surface of the suspended solid without the need to provide a substantial "encapsulating" layer in the form of a "network" to "trap" the solid particle. There is a clear economic advantage in reducing the quantity of polymeric stabiliser used in the formulation. Furthermore, we have found that reducing the quantity of polymeric stabiliser may minimise the unproductive cross-linking of the polymeric stabiliser by reaction with the cross-linking agent in the body of the liquid phase as opposed to on the particle surface. Whilst the cross-linking may have the effect of slightly increasing the overall particle size in the suspension, in general this effect, if it exists at all, is relatively small. We have found that the average particle size in the suspension normally remains well within preferred limits, for example below about 10 microns and more particularly below about 5

microns even after cross-linking. In contrast with the pigments that are the primary subject of US 6262152, certain agrochemicals have a small but finite solubility in the liquid medium. This may have adverse consequences for agrochemicals that are able to undergo an alteration of physical state, such as crystallisation. In particular, suspension concentrates of agrochemicals may become destabilised by a mechanism that involves transport of agrochemical into the liquid medium where the agrochemical may crystallise to form particles, which by virtue of size or shape may adversely affect the robustness and the bioperformance of the formulation.

The liquid medium is preferably an aqueous medium.

In one embodiment of the present invention the suspended solid, for example the suspended agrochemical, is present as a suspension concentrate in which the particulate solid is suspended directly in water. Typical examples of agrochemicals which are substantially insoluble in water and are formulated as aqueous suspension concentrates include azoxstrobin, picoxystrobin, abamectin, chlorthalonil, thiamethoxam, atrazine, simazine, ametryn, fluometuron, flutriafol, diafenthiuron, chlorothalanil, napropamide, nicosulfuron, sulcotrione and captan.

The scope of the present invention is not however limited to simple suspension concentrate formulations and includes for example suspoemulsions in which a suspension concentrate is formulated with an oil-in-water emulsion. The reactive polymeric surfactant may be cross-linked to stabilise either the suspended solid particle (in accordance with the present invention) or the dispersed phase of the emulsion (in accordance with our copending application PCT/GB02/02744) or both. It is a particular advantage that effectively the same surfactant may be used to stabilise both the suspended solid and the dispersed emulsion phase, even if in one instance it is cross-linked and in the other it is not.

The reactive polymeric surfactants for use in this invention (also referred to herein as polymeric stabilisers) generally have three moieties - a hydrophilic moiety, a hydrophobic moiety and a moiety that possesses reactive or cross-linking ability with respect to the one or more substances contained in the liquid phase of the suspension and capable of undergoing a cross-linking reaction with said functional group. When these surfactants are used with a particulate solid dispersed in a predominantly aqueous medium the hydrophobic moiety adsorbs strongly to the surface of the particulate solid while the hydrophilic moiety associates strongly with the aqueous medium, thereby conferring colloidal stability upon the suspended

solid. The cross-linking moieties enable the surfactant to become cross-linked by reaction with the cross-linking substance contained in the liquid medium, while the colloid stabilizing moieties of the surfactant provide surface-active properties to the thus cross-linked entity.

The surfactants for use in this invention are selected from certain random graft copolymers and certain block copolymers. It should be noted that the random graft copolymers and block copolymers for use in the present invention are surfactants in their own right which are then bound at the particle interface by reaction of the cross-linking moiety.

The properties of these surface active agent materials are determined by the composition and quantity of their hydrophobic and hydrophilic components.

The compositions and methods of preparation of polymeric surfactants are many and varied. A review of such materials is given in the text by Piirma: Polymeric Surfactants, Surfactant Science Series 42, (Marcel Dekker, New York, 1992). The two main classes of polymeric surfactants are those prepared as hydrophilic-hydrophobic blocks and those prepared as combs of hydrophilic arms attached to a hydrophobic backbone, and vice versa. Such hydrophobic-hydrophilic polymers have been termed "amphipathic" or "amphiphilic". Adsorption to the suspended solid is maximised where the surfactants have a high propensity to adsorb on the solid surface and have little or no propensity to micellise in the continuous phase.

In general, polymeric surfactants may be made by modifying previously prepared polymers or by polymerisation in a single step or stepwise manner. For example block co-polymers can be made by (i) the controlled stepwise polymerisation of firstly hydrophobic and secondly hydrophilic monomers, or the reverse of this process, or by (ii) coupling together pre-formed hydrophobic and hydrophilic materials of suitable molecular weight. Graft copolymers can be made by (i) graft polymerisation of hydrophilic monomers or macromonomers to a hydrophobic backbone, or the reverse of this process, or by (ii) coupling pre-formed hydrophobic or hydrophilic materials of suitable molecular weight to a polymer backbone which is a hydrophilic or hydrophobic backbone, respectively or by (iii) randomly copolymerising macromonomers that have hydrophilic pendant chains with hydrophobic monomers or copolymerising hydrophobic macromonomers with hydrophilic monmers.

The preferred preparative method for any given composition will depend on the nature and properties of the starting materials. For example, the reactivity ratios between certain monomers may limit the amount of a particular hydrophilic monomer that can be radically co-polymerised with hydrophobic monomers and visa versa.

In one embodiment, the polymeric stabilisers for use in this invention contain two types of units: a) hydrophobic units, which themselves contain cross-linking moieties; and b) hydrophilic units which provide colloid stabilizing and other surface-active properties. The polymeric stabilisers for use in this invention generally comprise two types, namely random graft copolymers and block copolymers.

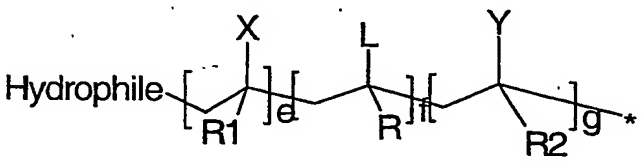
The polymeric stabilisers for use in this invention are composed of a plurality of vinylic monomers. Some of these, as discussed below, contain functional groups ("cross-linking groups") that are capable of undergoing a nucleophilic or condensation reaction with moieties or groups present in a variety of materials contained in the liquid phase.

The random graft copolymers have a hydrophobic "backbone" and hydrophilic "arms", whereas the block copolymers have hydrophobic and hydrophilic segments in which the hydrophobic segment contains the cross-linking element.

The reactive polymeric surfactants for use in the present invention may contain more than one type of monomer capable of undergoing a cross-linking reaction. For example the copolymers may comprise both amine and carboxylic acid containing monomers. The copolymers may alternatively comprise both hydroxyl and carboxylic acid containing monomers.

The polymeric stabilisers for use in this invention may be made as known in the art either by modifying previously prepared polymers or by production through polymerization in a single step or in a stepwise manner.

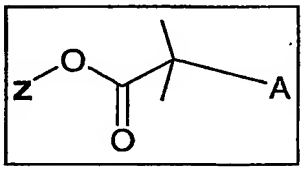
The reactive polymeric surfactants for use in this invention, both random graft copolymers and block copolymers, may be represented by the formula:



Formula (I)

where "Hydrophile", when present, is the residue of a hydrophilic initiator group; R1, R and R2 are independently H or methyl; X is a hydrophilic moiety; L is a moiety containing a cross-linking group; Y is a hydrophobic moiety; the value of e is from 0.005 to 0.35; the value of f is from 0.05 to 0.4 and the value of g is from 0.10 to 0.90. When the surfactant is a random graft copolymer, the units e, f and g are randomly distributed and when the surfactant is a block copolymer the units f and g are contained in a hydrophobic block and the units e are contained in a hydrophilic block. The expression "the units e, f and g" as used above indicates the moieties in square brackets preceding the subscripts e, f and g respectively in the above formula. Each unit e, f and g is derived from a corresponding vinylic monomer and, as noted above, each unit type e, f and g may comprise one or more different monomers. When R1, R and R2 respectively are hydrogen, the relevant monomer is an acrylate or styryl type monomer and when R1, R and R2 respectively are methyl, the relevant monomer is a methacrylate type monomer. A styrene type monomer (useful for example in unit e) has R1 as H and X as a hydrophilically substituted phenyl derivative. The values of e, f and g are determined essentially by the ratios of the monomers reacting to form the units e, f and g respectively.

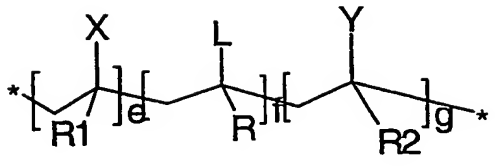
If a hydrophilic initiator is used, the polymer will start with a hydrophilic group designated "Hydrophile" in Formula I. A typical hydrophilic initiator has the formula II



II

wherein A is a group such as bromine or chlorine that under certain conditions, such as in the presence of a transition metal complex, may be activated such that vinylic monomer units are inserted into the carbon-A bond and Z is a methoxy-polyethylene glycol group. It will be appreciated that the group "Hydrophile" in Figure I is joined with one or more of the units e when e is present in a di-block copolymer. The units e are randomly distributed in a comb copolymer.

If a hydrophobic initiator is used it will be appreciated that the reactive polymeric surfactant takes the formula IA



IA

It is preferred that in formula (I):

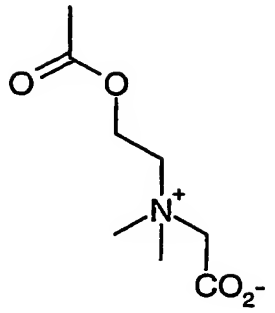
(i) the group e is derived from one or more monomers which is a methacrylate derivative (when R1 is methyl and the derivative function is -X) or is an acrylate derivative (when R1 is hydrogen and the derivative function is -X) or is a styrene derivative (when R1 is hydrogen and X is phenyl substituted with the hydrophilic moiety) wherein said derivative carries a hydrophilic moiety selected from $-SO_3^-$, polyethylene glycol optionally end-capped with C1-C4 alkyl; -COOH or a salt thereof; carboxybetaine; and sulfobetaine; a quaternary ammonium salt $-N^+R^3{}_3C^-$ where R^3 is H or C1-C4 alkyl or $-CH_2CH_2OH$

(ii) the group f is derived from one or more monomers which is a methacrylate derivative (when R is methyl and the derivative function is -L) or is an acrylate derivative (when R is hydrogen and the derivative function is -L) or is a styrene derivative (when R is hydrogen and L is phenyl substituted by the cross-linking group) wherein said derivative carries a cross-linking group selected from –OH, including for example propylene glycol; -NHA where A is hydrogen or C_1-C_4 alkyl; and -COOH or a salt thereof; and

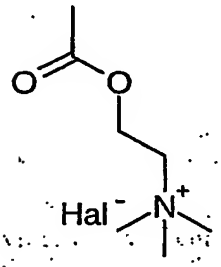
(iii) the group g is derived from one or more monomers which is a methacrylate derivative (when R_2 is methyl and the derivative function is -Y) or is an acrylate derivative (when R_2 is hydrogen and the derivative function is -Y) or is a styrene derivative (when R_2 is hydrogen and Y is phenyl optionally substituted by a hydrophobic group) wherein said derivative is or carries a hydrophobic moiety selected from $-CO\text{-}O\text{-}(\text{-}Si(CH_3)_2O\text{-})_n\text{-}H$ wherein n is from 3 to 20; -CO-O-polypropylene glycol; –CO-O-A wherein A is a C_1-C_{12} alkyl group, cycloaklyl group, alkylcycloalkyl group, aralkyl group or alkylaryl group; and -CONHB wherein B is a C_5-C_{12} alkyl group.

It is especially preferred that the unit e is derived from one or more of the following monomers:-

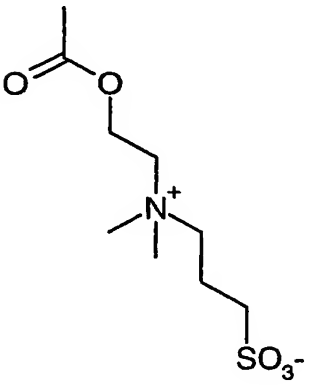
DMMAEA betaine*: 2-(N,N-Dimethyl-N-(2-methacryloxyethyl) ammonium)ethanoic acid, wherein R1 is methyl and –X has the formula



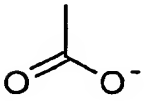
QuatDMAEMA: 2-(Trimethylammonium)ethyl methacrylate salt ;
wherein R1 is methyl and –X has the formula wherein Hal^- is a suitable anion such as halide, for example iodide or chloride



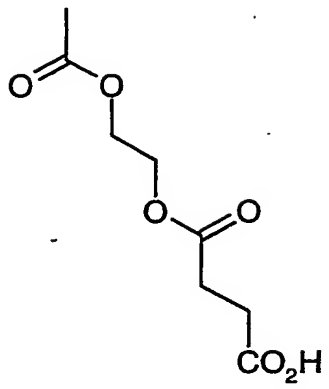
DMMAPSA betaine: 3-(N,N-Dimethyl-N-(2-methacryloxyethyl) ammonium)propyl-sulphonic acid; wherein R1 is methyl and –X has the formula



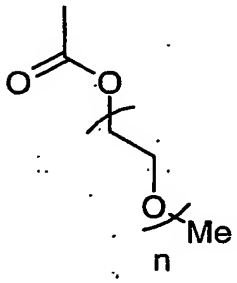
NaMAA*, the sodium salt of methacrylic acid, wherein R1 is methyl and –X has the formula



MAOES* mono-2-(Methacryloyloxy)ethyl succinate wherein R1 is methyl and –X has the formula

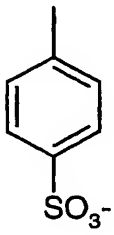


PEGMA: Mono-methoxy poly(ethylene glycol) mono-methacrylate; wherein R1 is methyl and –X has the formula wherein n indicates the average degree of polymerisation of the polyethylene glycol chain and is typically from 5 to 75



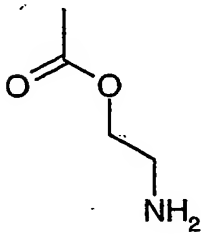
SSA: Styrene-4-sulfonic acid;

wherein R1 is hydrogen and –X has the formula

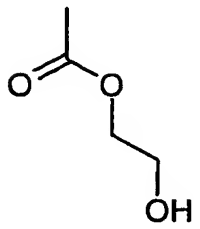


It is preferred that the unit f is derived from one or more of the following monomers:

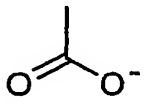
AEMA: 2-Aminoethyl methacrylate wherein R is methyl and L is the group



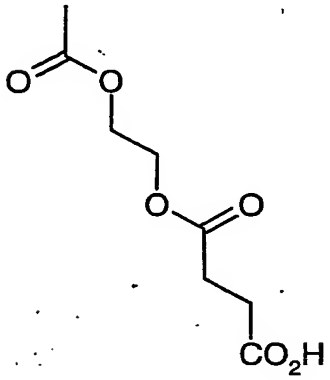
HEMA: 2-Hydroxyethyl methacrylate, wherein R is methyl and L is the group



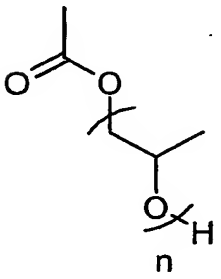
NaMAA* wherein R is methyl and L is the group



MAOES*: wherein R is methyl and L is the group

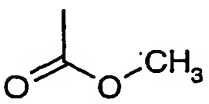


PPGMA*; Poly(propylene glycol) mono-methacrylate wherein R is methyl and L is the group

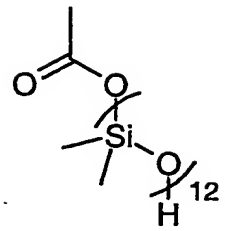


wherein n indicates the degree of polymerisation of the propylene glycol and is preferably from 5 to 50

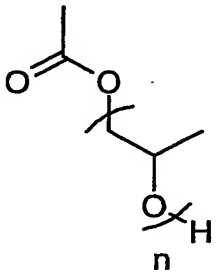
It is preferred that the unit g is derived from one or more of the following monomers: methyl methacrylate wherein R is methyl and Y is the group:



PDMSMA: Poly(dimethylsiloxane) mono-methacrylate, typically with an average molecular weight of 1000 wherein R is methyl and Y is the group



PPGMA*; Poly(propylene glycol) mono-methacrylate wherein R is methyl and L is the group wherein n indicates the degree of polymerisation of the propylene glycol and is preferably from 5 to 50. In general a relatively greater chain length is preferred in order to provide the necessary hydrophobic character.



It will be noted that certain monomers (marked with an asterisk) occur in more than one group and for example have hydrophilic groups X that may if desired be used to provide cross linking (i.e. may also act as a moiety L). For example salts of carboxylic acids may be used for stabilisation, when the monomers bearing $-CO_2X$ groups are incorporated into the hydrophilic part of the surfactant. Free carboxylic acids may however be used for cross-linking using aziridine or carbodiimide chemistry, when the monomers bearing the $-CO_2H$ groups would be incorporated into the hydrophobic part of the surfactant. Clearly if $-CO_2H$ is used for cross-linking it cannot be used for stabilisation. Where two different groups in the surfactant are capable of reacting in the cross linking chemistry, but have very different reactivity it is possible to use the less reactive group for stabilisation e.g. carboxylates in the hydrophile and hydroxyls in the hydrophobe sections. One skilled in the art is readily able to select the conditions such that a given group undergoes a cross-linking reaction or alternative conditions such that it does not.

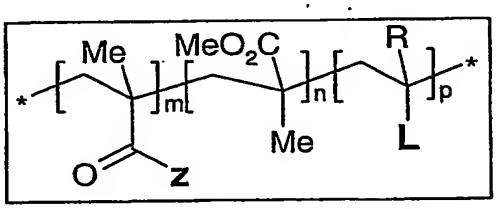
Further examples of monomers which can be used to form unit "e" (and provide corresponding values of R1 and X) include 4-vinylbenzyl trimethyl ammonium chloride, 2-N-morpholinoethyl, 2-methacryloxyethylphosphonate methacrylate, 2-acrylamido-2-methylpropane sulphonic acid.

Further example of monomers which can be used to form unit "f" (and provide corresponding values of R and L) include 2-methoxy-4-vinylphenol, 4-vinylbenzyl alcohol, 4-vinylphenol, 2,6-dihydroxymethyl-4-methoxystyrene, 3,5-dimethoxy-4-hydroxystyrene, 2-hydroxy-3-methacryloxypropyl trimethyl ammonium chloride, 3-chloro-2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, 2-hydroxy-3-phenoxypropyl methacrylate, diethylene glycol mono-methacrylate, 2,3-dihydroxypropyl methacrylate, 2-methacryloxyethyl glucoside, sorbitol methacrylate, caprolactone 2-methacryloxyethyl ester, 4-hydroxybutyl methacrylate, 2-hydroxypropyl methacrylate, 4-aminostyrene, 2-(iso-propylamino)ethylstyrene, 4-N-(vinylbenzyl)aminobutyric acid, 3-(N-styrylmethyl-2-aminoethylamino)-propyltrimethyoxysilane hydrochloride, N-(3-methacryloxy-2-hydroxypropyl)-3-aminopropyltriethoxysilane, 4-vinylbenzoic acid, 4-((3-methacryloxy)propoxy)benzoic acid, mono-(2-(methacryloxy)ethyl)phthalate.

Further example of monomers which can be used to form unit "g" (and provide corresponding values of R_2 and Y) include acrylate (R_2=H) or methacrylate (R_2=methyl) derivatives wherein Y is COOR, and R is alkyl, cycloalkyl, aralkyl or alkaryl, or poly(dimethylsiloxane), vinyl esters, vinyl halogens, styrene or optionally substituted styrenes.

As noted above, Formula (I) describes both random graft copolymer stabilisers and block copolymers. Random graft copolymer stabilisers useful in this invention have a hydrophobic backbone and hydrophilic "arms." A typical structure is illustrated below which includes a polymethyl methacrylate backbone containing methoxy-polyethylene glycol methacrylate and hydroxyethyl methacrylate moieties. This structure is illustrated as Formula III

FORMULA (III)



In this structure, Z is a hydrophilic group such as methoxy-PEG in which PEG (polyethylene glycol) stands for a number of ethylene oxide units $(C_2H_4O)_q$. Z may

alternatively be derived from a monomer which is another (meth)acrylate ester or functionalised (meth)acrylamide derivative that contains a hydrophilic group such as a sulphonate, for example 2-acrylamido-2-methylpropane sulphonic acid. Mixtures of groups Z may also be used.

L in the above structure is a cross-linking group such as $-CO_2CH_2CH_2OH$, in the monomer hydroxyethyl (meth)acrylate (where R = H or Me). L may alternatively be derived from a monomer which is another (meth)acrylate ester or functionalised (meth)acrylamide derivative containing a cross-linking group such as found in N-(2-hydroxylpropyl) methacrylamide or a substituted styryl derivative that contains a cross-linking group such as SH or OH or NHA in which A is hydrogen or C_1-C_4 alkyl, illustrated by the structure $-C_6H_4-CH_2NH_2$.

The values of *m*, ranges from about 0.05 to 0.35 and preferably 0.05 to 0.30, the values of n range from 0.13 to 0.90 and preferably from 0.50 to 0.80, and the values of p range from 0.02 to 0.35 and preferably from 0.02 to 0.20. The polymers are random graft (comb) copolymers because the units indicated as *m*, *n*, and *p* can be distributed in any order in the chain of the molecule. It will be appreciated that the moieties –CO-Z form the hydrophilic "arms" of the random graft copolymers and the remaining units form the hydrophobic backbone which also contains the cross-linking moieties L.

It will be appreciated that formula (III) is a more specific form of Formula (I) and that the monomers listed above in respect of formula (I) wherein –X has a carboxyl structure may be used to provide the relevant group –CO-Z in formula (III).

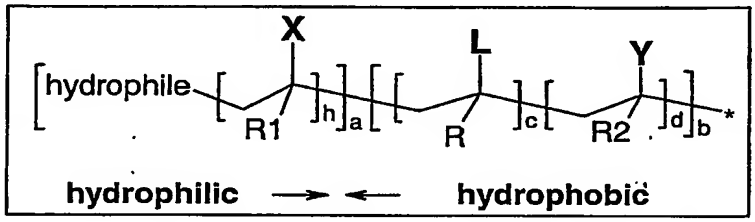
In general, random graft copolymers for use in this invention can be prepared by typical methods of preparing known random graft copolymeric surfactants or similar materials. These methods include (a) by graft polymerisation of hydrophilic monomers to a hydrophobic backbone or (b) the reverse of process a, or (c) by chemically converting suitable monomers that have been copolymerised with hydrophobic backbone monomers. Polymers having similar surfactant properties to those of graft copolymers can be made by randomly copolymerising hydrophilic and hydrophobic monomers.

The preferred method of preparation for any given graft or similar copolymer will depend on the nature and properties of the starting materials. For example, the reactivity ratios between certain monomers may limit the amount of a hydrophilic monomer that can be radically copolymerised with hydrophobic backbone monomers.

Some novel amphipathic graft copolymers and methods of preparation are shown in PCT application WO 96/00251.

Preferred block copolymers for use in the present invention are comprised of a hydrophilic A block, which in turn is comprised of a hydrophile and/or hydrophilic monomer(s) ($-CH_2CR^1X-$), that is adjoined to a hydrophobic B block which is comprised of randomly copolymerised hydrophobic monomer(s) ($-CH_2CR^2Y-$) and cross-linking units ($-CH_2CH_2CRL-$). These are illustrated as Formula IV which is a more specific version of formula (I).

FORMULA (IV)



The hydrophilic A block may be made from one or more monomers which upon polymerisation and then optionally further chemical modification afford water-soluble polymers. The group designated "hydrophile" in Formula (IV) has the same meaning as given above in respect of Formula (I) and represents the residue of a mono-methoxy (polyethyleneglycol) derived initiator. The monomers may be nonionic or may be positively or negatively charged as part of the surfactant composition

In the above Formula IV, values for units *a* and *b* range from about 0.3 to about 0.7, and the values for *c* and *d* range from about 0.05 to about 0.35 and preferably from about 0.05 to about 0.25 and about 0.75 to about 0.95, respectively. The value of *c* is preferably selected so as to balance the hydrophobicity of the surfactant with the reactivity of the cross-linking group; a preferred range for c is from about 0.1 to 0.25.

Units *c* and *d* (i.e. the unit within the square brackets before the subscripts *c* and *d* respectively) comprise the hydrophobic backbone of the block copolymer surfactants and are, for example, derived from acrylate, methacrylate or styryl structures. Unit *d*, for instance, may be an acrylate ($R_2 = H$) or methacrylate (R_2 = methyl) derivative wherein Y is COOR, and R is alkyl, cycloalkyl, aralkyl or alkaryl. The choice for Y determines the hydrophobicity of this unit of the surfactant. For instance, if Y is $CO_2C_8H_{17}$ and R_2 is hydrogen or methyl,

this unit of the surfactant will be very hydrophobic. If, on the other hand, Y is $COOCH_3$ and R_2 is hydrogen, the unit is less hydrophobic. If *d* is a styryl unit (i.e., Y is phenyl and R_2 is hydrogen) the unit will be very hydrophobic.

Units *c* contain cross-linking groups within the moiety L and branching groups R (which are usually hydrogen or methyl). Cross-linking groups within the moiety L are preferably functional groups of esters that must be capable of reacting with cross-linking substances contained in the liquid phase such as isocyanates. Cross-linking groups within L preferably contain reactive groups such as -OH, -SH, $-CO_2H$ or –NHA, where A is hydrogen or C_1-C_4 alkyl. Preferred units *c* include those derived from the monomers hydroxyethyl methacrylate (R = methyl, L = $COOCH_2CH_2OH$), methacrylic acid (R = methyl, L = $-CO_2H$), (mono-2-(methacryloyloxy)ethyl succinate (R = methyl, L = $COOCH_2CH_2OCOCH_2CH_2-CO_2H$), or 2aminoethyl methacrylate (R = methyl, L = $COOCH_2CH_2NH_2$).

Units *a* comprise hydrophilic moieties, preferably acrylate or methacrylate derived moieties, and, if present, the initiator derived hydrophile is a preferably a water-soluble nonionic polymer such as mono-methoxy-poly(ethylene glycol). Moiety X is preferably a hydrophilic moiety such as that in 2-(trimethylammonium)ethyl methacrylate halide, 2-(N,N-dimethyl-N-(2-methacryloxyethyl) ammonium)ethanoic acid, 3-(N,N-dimethyl-N-(2-methacryloxyethyl) ammonium)propyl-sulphonic acid or styrene-4-sulfonic acid or 2-acrylamido-2-methylpropane sulphonic acid (AMPS).

Examples of water-soluble nonionic polymers suitable for use as the "hydrophile" group include, *inter alia,* poly(ethylene oxide) ("PEO"), poly(acrylamide), poly(vinyl pyrrolidone) ("PVP"), poly(methyl vinyl ether). PEO and PVP cannot be used in formulations containing polyacids that form complexes with their functional groups. The structure of the water-soluble non-ionic polymer may be linear or branched, including comb-shaped. Polymers such as polyethoxy (meth)acrylate, poly(vinyl alcohol), poly(ethylene imine), and poly(vinylamine) contain reactive groups that would react with isocyanates such as those used for cross-linking are not preferred for construction of the hydrophilic A block.

Examples of negatively charged monomers that may be included in these polymers include, *inter alia*, those made from acrylic acid, methacrylic acid, beta-carboxyethylacrylic acid, mono-2-(methacryloyloxy)ethyl succinate, 4-vinylbenzoic acid, itaconic acid, vinyl sulphonic acid, 2-sulphoethyl methacrylate, 2-acrylamido-2-methylpropane sulphonic acid

(AMPS), 4-styrene sulphonic acid, and their respective salts. Note that polyacrylic acid is not preferred for use in combination with methoxy-PEO containing "hydrophile" groups since association will occur between them. However, (meth)acrylic acid could be used as a component of the hydrophobic B block since it would be present in comparatively low amounts and does not associate with PEO.

Examples of positively charged monomers that may be included in these polymers include, *inter alia,* those made from diallyldimethyl ammonium salts, quaternary salts of dimethylaminoethyl methacrylate (DMAEMA) and of dimethylaminoethyl acrylate.

The hydrophobic B block may be made from one or more monomers that upon polymerisation afford a water-insoluble polymer that may be strongly adsorbed to the surface of the discontinuous phase. Examples of suitable monomers include, *inter alia,* acrylate esters, methacrylate esters, vinyl esters, vinyl halogens, styrene or substituted styrenes.

The cross-linking units may be co-polymerised at a desired mole ratio with other monomers to make the hydrophobic B block. Typical ratios vary from two to ten units of hydrophobic monomers to one cross-linking units. The chosen ratio depends on the molecular weights and on the hydrophilic-hydrophobic balance of the hydrophobic and cross-linking units. The structure of the cross-linking units chosen depends on the desired chemistry of reaction between the surfactant and the cross-linking component(s) contained in the continuous phase.

A cross-linking substance (the reaction partner) is used in the liquid continuous phase of a suspension of the present invention where it reacts with the appropriate functional groups on the reactive polymeric surfactant that is adsorbed on the surface of the solid particles. Many cross-linking chemistries are known. When the cross-linking moiety L contains a hydroxyl or thiol reactive group, suitable reaction partners may have as their corresponding reactive group, for example, isocyanate, ester or epoxide. When the cross-linking moiety L contains an amine reactive group then suitable reaction partners may have as their corresponding reactive group, for example, isocyanate, acetoacetoxy, aldehyde, acrylate, vinylsulphone or epoxide. When the cross-linking moiety L contains an acid reactive group then suitable reaction partners may have as their corresponding reactive group, for example, isocyanate, aziridine or carbodiimide. The preferred cross-linking/partner combinations of this invention are hydroxyl-isocyanate, amine-isocyanate and acid-carbodiimide. The cross-linking group may react with more than one type of reaction

partner compound contained in the liquid phase that are capable of undergoing cross-linking reactions with said groups. The reaction partner may contain more than one type of functional group capable of undergoing reaction with the reactive cross-linking groups on the polymeric surfactant.

The functionality of the substance contained in the liquid phase capable of reacting with the cross-linking groups on the surfactant is suitably equal to or greater than two. The invention is not limited by the structure of the substance provided that the substance reacts with the cross-linking groups on the polymeric surfactant. The substance may be soluble in the liquid medium (preferably an aqueous medium) or may be dispersed in the liquid medium, for example as a water-insoluble oil dispersed in an aqueous medium.

For example, in one embodiment of this invention, when the aqueous medium contains isocyanates as reaction partner, the cross-linking groups on the polymeric stabiliser are primary amino, secondary amino, hydroxyl, thiol or carboxyl respectively. Hydroxyl and amino groups are preferred and primary and secondary amino groups are most suitable. Tertiary amino groups may catalyse isocyanate reactions but do not usually form stable reaction products. When more than one functional group on the reactive polymeric surfactant, L, is present the groups may be the same or differently chemically functional. Reactions with isocyanates are illustrated here using generic structures.

Carboxylic groups may be introduced using for example mono-2-(methacryloyloxy) ethyl succinate, acrylic acid, methacrylic acid, beta-carboxyethylacrylic acid, 4-vinylbenzoic acid and itaconic acid. Enhanced adsorption to the particle surface may be accomplished if the pH of the aqueous medium is first adjusted above the pKa of the acid, i.e., the acid is in the salt form, which favours water solubility, and then subsequently, but before or during cross-linking, reduced to below the pKa of the acid, which will reduce water solubility. Carboxylic acids react with isocyanates to form mixed anhydrides that rapidly eliminate carbon dioxide with the formation of carboxylic amides:

$$RNCO + R^1CO_2H \rightarrow [RNHCOOCOR^1] \rightarrow R^1CONHR + CO_2$$

Hydroxyl groups may be introduced using hydroxethyl methacrylate, N-(2-hydroxypropyl)methacrylamide, or poly(ethylene glycol)$_n$ monoethacrylate. Amino groups may be introduced using 2-aminoethyl methacrylate hyrochloride,

N-(3-aminopropyl)methacrylamide hydrochloride or 2-(tert-butylamino)ethyl methacrylate. Thiol, hydroxyl and amino groups react with isocyanates to form respectively thiocarbamate, urethane, and urea linkages:

$$RNCO + R^1SH \rightarrow RNHCO\text{-}S\text{-}R^1 \quad \text{thiocarbamate linkage}$$
$$RNCO + R^1OH \rightarrow RNHCO\text{-}O\text{-}R^1 \quad \text{urethane linkage}$$
$$RNCO + R^1NH \rightarrow RNHCO\text{-}N\text{-}R^1 \quad \text{urea linkage}$$

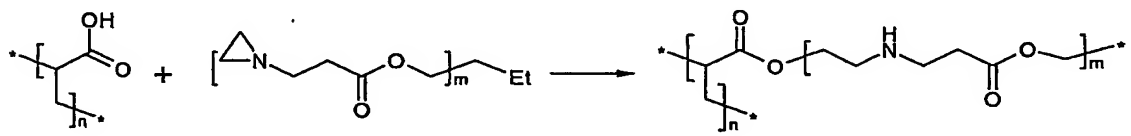
In a further embodiment of the invention, the nature of the cross-linking groups may be altered, or cross-linking groups may be introduced by post-reaction of the copolymer. For example, carboxylic groups may be iminated to make polyimine combs.

$$-CO_2H + \text{ethyleneimine} \rightarrow -CO_2\text{-}[CH_2CH_2NH]_n\text{-}H$$

Amine groups react with isocyanates in the manner described above.

The reactivity of the functional group with the isocyanate influences the rate at which the cross-linking takes place. For example, isocyanates typically react much faster with amines than with alcohols or acids. When hydrolytically sensitive cross-linking agents, such as those containing isocyanate groups, are added to the aqueous medium it is an advantage that a rapid reaction between the functional group on the reactive surfactant and the reactive compound contained in the liquid medium takes place in preference to hydrolysis.

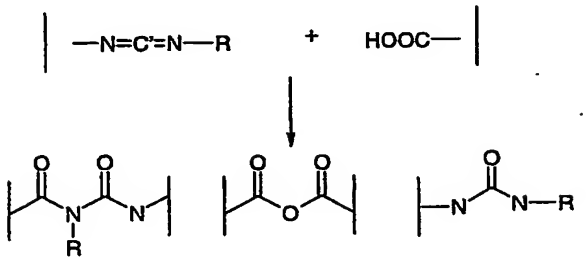
Multi-functional aziridines such as CX-100 available from Avecia Neo Resins (structural formula shown below, m=3) may be used as the reactive compound contained in the liquid medium if carboxylic acid functional monomers are incorporated into the polymeric surfactant. Aziridines react with carboxy groups in their free acid but not salt forms.



CX-100

Poly(Carbodiimides) such as CX-300 available from Avecia NeoResins may also be used as the reactive compound contained in the liquid medium if carboxylic acid functional monomers are incorporated into the polymeric surfactant . Reaction between the carboxylic acid and the carbodiimide is conventionally believed to result in three types of products as

illustrated below. The N-acyl urea and urea products are stable while the anhydride may be hydrolysed to two carboxylic acids.



As examples of suitable isocyanates for use in this invention there may be mentioned, inter alia, m-phenylene disisocyanate, 1-chloro-2,4-phenylene diisocyanate; 4,4'-methylenebis(phenyl isocyanate); 3,3'dimethyl-4,4'-biphenylene diisocyanate 4,4'-methylenebis(2-methylphenyl isocyanate); 3,3'dimethoxy-4,4'biphenylene diisocyanate; 2,4-tolylene diisocyanate; 2,6-tolylenedi isocyanate; 5,5-tetramethyl-4,4'-biphenylene diisocyanate; isophorone diisocyanate; hexane-1,6-diisocyanate;tetramethylene xylene diisocyanate.

As examples of suitable materials for crosslinking hydroxyl groups on the reactive polymeric surfactants we would mention, inter alia, divinylsulphone and glycerol triglycidyl ether. As examples of suitable materials for cross-linking amine groups on the reactive polymeric surfactants we would mention, inter alia, glycerol triglycidyl ether; glycerol propoxylate triglycidyl ether; trimethylolpropane triacrylate; trimethylolpropane propoxylate triacrylate; glutaric dialdehyde; 2-(acetoacetoxy) ethyl acrylate and 1,4-butandiol diacetoacetate.

It is preferred to use a stoichiometric or greater equivalent of functional groups on the cross-linking material relative to the number of cross-linkable functional groups on the reactive polymeric surfactants. As an example, for 'n' amine groups on the RPS a similar or greater number 'n' of isocyanate groups would be added from the material in the aqueous phase. Excess functional groups of the aqueous phase material may be used to compensate for any hydrolysis that may occur before the desired cross-linking reaction takes place.

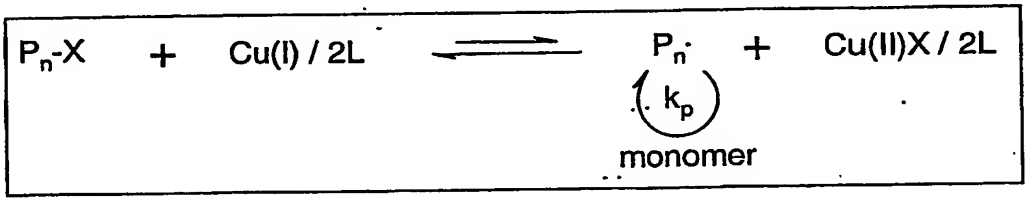
Block copolymers may be prepared by methods known in the art. These tend to involve either anionic or group transfer polymerisation methods that give fine control over molecular weights, poly-dispersities (PDi) and polymer architecture. Preparative conditions for these methods are very demanding, for example, the need for low temperatures, the use of

rigorously anhydrous solvents, and of extremely pure reagents. In addition, the use of functional monomers often requires employment of protecting group chemistry. These factors have limited the widespread commercial exploitation of the technologies.

By contrast 'conventional' radical polymerisation technology has been extensively exploited due in part to the availability of a broad range of monomers and functionalities, and to the robustness of the technique that tolerates a wide range of operating conditions. Polymerisation may be done in both organic and aqueous media. However limitations on the conventional technology are imposed by the difficulty in controlling product architecture and the lack of selectivity of radical reactions. The limitations are reduced or eliminated in controlled radical polymerisation (CRP) methods. Several such CRP methods are known, including those mediated by metal, sulphur and nitroxide chemistries. Atom transfer radical polymerisation (ATRP) is an example of CRP mediated by metal chemistry.

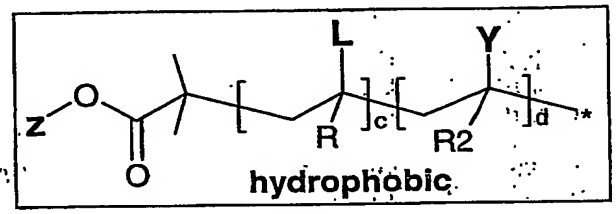
We have found that ATRP, a process which allows precise control over the polymer composition and molecular weight, is particularly useful for preparing reactive polymeric surfactants for use at relatively low concentration in the present invention. This method is tolerant of monomer type [styrene and (meth)-acrylic derivatives], impurities in reagents and to the presence of water and the use of functional monomers often does not require protection/deprotection chemistry. The resultant polymers generally provide better suspensions when used at lower concentration compared with polymers prepared using techniques such as those disclosed in US 6262152. Such polymers made by controlled radical polymerisation generally have lower polydispersities than comparable polymers made by non-living radical methods. The control thus minimises the amount of low molecular weight tail in the molecular weight distribution. The strength of adsorption of surfactants to hydrophobic surface depends on the number of hydrophobic units in the surfactant that are available for adsorption. Assuming comparable composition over the molecular weight range, higher molecular weight chains will have more such hydrophobic units and will bind more strongly than low molecular weight chains. For the minimum effective ratio of surfactant to liquid medium the amount of 'unbound' material in the liquid medium is thus minimised. This then minimises or removes material that could act as carriers for material transfer and potential crystallisation, particularly for example in the case of a suspended particulate agrochemical.

One system for carrying out ATRP is described by Coca *et al* in *J Polym Sci: Part A Polym Chem*, Vol 36, 1417-1424 (1998) "ATRP employs a Cu(I) halide, which is complexed with ligands (often bidentate), to form a "CuX/2L" complex. Halogenated initiators are used for polymerisation. The Cu(I) complex reversibly activates dormant polymer chains (and the initiator) by transfer of the halogen end groups as shown in Scheme 1."



Scheme 1

The following structures further illustrate polymers for use in this invention.



FORMULA (V)

In formula (V) L, R, R^2, Y, c and d have the definitions given previously in respect of the polymer of formula (IV) and Z is a hydrophilic group such as methoxy-PEG. For example the hydrophilic segment containing [Z-OCOCMe$_2$-] may have Z as methoxy-PEG of Mw 350-10000, preferably 350-4000. Polymers of the type illustrated by Formula V are given in the Examples where the hydrophilic segment is provided by a methoxy poly(ethyleneglycol) macroinitiator (ZO$_2$CCMe$_2$-). Examples are given in which the unit c is MAOES and the unit D is MMA and in which the unit c is HEMA and the unit d is MMA.

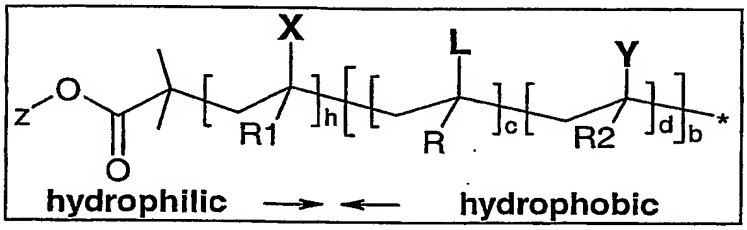
The hydrophobic segment containing -[CH$_2$CYR^2]- may be single or mixed monomers selected from acrylates (R^2 = H, Y = -CO$_2$A where A is a C$_1$-C$_{12}$ optionally substituted hydrocarbyl moiety); methacrylates (R^2 = Me, Y = -CO$_2$A where A is a C$_1$-C$_{12}$ optionally substituted hydrocarbyl moiety); alkyl acrylamides (R^2 = H or Me, Y = -CONHB where B is a C$_5$-C$_{12}$ alkyl group); styryl (R^2 = H or Me, Y = phenyl or substituted phenyl).

The cross-linking unit(s) -[CH$_2$CLR]- may be for example single or mixed monomers selected from:-

- amine functional monomers such as 2-aminoethyl methacrylate hyrochloride, N-(3-aminopropyl)methacrylamide hydrochloride, 2-(tert-butylamino)ethyl methacrylate
- hydroxy monomers such as N-(2-hydroxypropyl)methacrylamide, hydroxethyl methacrylate, or poly(ethylene glycol)$_n$ monoethacrylate
- carboxylic monomers such as acrylic acid, methacrylic acid, beta-carboxyethylacrylic acid, 4-vinylbenzoic acid, itaconic acid or iminated derivatives of these monomers once polymerised.
- monomers such as glycidyl (meth)acrylate which can be converted to reactive functional groups by reaction with, for example, alkylamines

Especially preferred cross-linking units for Formula IV/V include amine functional monomers such as 2-aminoethylmethacrylate; hydroxy monomers such as2-Hydroxyethyl methacrylate, poly(ethylene glycol)n monoethacrylate, carboxylic monomers such as mono-2-(Methacryloyloxy)ethyl succinate and methacrylic acid;

In the case of some of the above block copolymers the hydrophilic A block may be introduced from a macro-initiator of defined structure [typically Z-OCOCMe$_2$Br] which is extended with appropriate amounts of hydrophobic (CH_2=CR_2Y) and cross-linking (CH_2=CRL) monomers. Alternatively, or in addition to the above, the initiator (which may not be a macro-initiator) may be chain extended with a hydrophilic monomer (CH_2=CR_1X) to generate the hydrophilic A block and thence with appropriate amounts of hydrophobic (CH_2=CR_2Y) and cross-linking (CH_2=CRL) monomers to generate the hydrophobic B block (or alternatively the groups CH_2=CR_1X, CH_2=CR_2Y, and CH_2=CRL may be randomly copolymerised to form graft copolymers).



FORMULA (VI)

The hydrophilic moiety [Z-OCOCMe$_2$-CH_2CR^1X-] may have Z as a C_1-C_3 alkyl or mono-methoxy-PEO group.

The vinylic monomners ($CH_2=CR_1X$) giving rise to the hydrophilic unit(s) may be single or mixed monomers selected from, *inter alia,* mono-methoxy-PEO-(meth)acrylate, acrylamide, vinyl pyrrolidone, 2-sulphoethyl methacrylate, 2-acrylamido-2-methylpropane sulphonic acid, 4-styrene sulphonic acid, quaternary salts of dimethylaminoethyl methacrylate (DMAEMA) and of dimethylaminoethyl acrylate or DMAEMA at acid pHs. Preferred monomers include 2-(trimethylammonium)ethyl methacrylate iodide, 2-(N,N-dimethyl-N-(2-methacryloxyethyl) ammonium)ethanoic acid, 3-(N,N-dimethyl-N-(2-methacryloxyethyl) ammonium)propyl-sulphonic acid or styrene-4-sulfonic acid .

The hydrophobic block -[CH_2CYR^2]- may be single or mixed monomers selected from the above list. The cross-linking unit(s) -[CH_2CLR]- may be single or mixed monomers selected from the above list. Optimum total molecular weight and the sizes of the blocks of the surfactants will depend on the nature of the monomers and on the active ingredient employed in the process. Molecular weights in general will range from about 1,000 to about 20,000. Preferred molecular weights are between about 5,000 to about 20,000. The cross-linking groups are incorporated at less than 100% level into the surfactant, preferably from about 2 to about 20 mole % of the hydrophobic B block. The nature of the polymeric surfactant will determine the medium in which it can be made and used. This will range from nonpolar solvents such as xylene through to polar solvents such as water. While surfactants having some solubility in both the discontinuous phase and the continuous phase are suitable for use in this invention, surfactants which have limited solubility in the bulk continuous phase and which adsorb strongly at the interface of the discontinuous phase are preferred. Hydrophobic monomers described as CH2=CRY units above, in general, adhere strongly to the discontiuous phase. Methyl methacrylate is suitably hydrophobic, while butyl acylate and styrene are even more hydrophobic.

The suspension of a particulate solid in a liquid medium, for example the preparation of a conventional suspension concentrate generally takes place by milling the solid in the presence of the liquid medium and a suitable surfactant. It is an advantage of the present invention that the reactive polymeric surfactants are effective dispersants when incorporated (prior to cross-linking) to assist the milling process and may subsequently be cross-linked to stabilise the suspension of the milled particle in the liquid medium.

Thus according to a further aspect of the present invention there is provided a process for the manufacture of a suspension of a particulate solid in a liquid medium which comprises the steps of

1. milling the solid in the presence of the liquid medium and a polymeric stabiliser having a hydrophilic moiety and a hydrophobic moiety and comprising a plurality of vinylic monomers, not being exclusively of vinylic esters or of their hydrolysed products, at least some of which contain functional groups capable of undergoing cross-linking nucleophilic or condensation reactions; and subsequently
2. reacting said polymeric stabiliser with one or more substances contained in the liquid phase and capable of undergoing a cross-linking reaction with said functional groups

wherein the ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended solid is no more than 1 part of polymeric stabiliser per 5 parts of suspended solid.

The substance capable of undergoing a cross-linking reaction is preferably added to the liquid phase after milling. It is preferred to allow the substance capable of undergoing a cross-linking reaction the opportunity to adsorb onto the solid suspended particles prior to cross-linking. Typically this will take from 5 seconds to 30 minutes.

The invention is illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated. The following abbreviations are used:

AEMA.HCl: 2-Aminoethyl methacrylate hydrochloride; from Sigma Aldrich.

tBAEMA: 2-(t-Butylamino)ethyl methacrylate, from Sigma Aldrich.

CX-100: Aziridine crosslinker; Avecia NeoResins

CX-300: Poly(carbodiimide) crosslinker; from Avecia NeoResins.

DETA: Diethylene triamine from Sigma-Aldrich

DHPMA: 2,3-dihydroxypropyl methacrylate, Rohm GMBH.

DMAEMA: 2-(Dimethylamino)ethyl methacrylate; from Sigma Aldrich.

QuatDMAEMA (PP): 2-(Trimethylammonium)ethyl methacrylate iodide or chloride where PP indicates that the monomer used was DMAEMA and the quaternisation reaction was carried out post-polymerisation using methyl iodide.

DMMAEA betaine: 2-(N,N-Dimethyl-N-(2-methacryloxyethyl) ammonium)ethanoic acid (prepared *via* a modification of the literature procedure; L. A. Mkrtchyan *et al.* Vysokomol. Soedin., Ser. B 1977, *19*(3), 214-16.

DMMAPSA betaine: 3-(N,N-Dimethyl-N-(2-methacryloxyethyl) ammonium)propyl-sulphonic acid; from Sigma Aldrich.

EDTA: Ethylenediaminetetraacetic acid; from Sigma Aldrich.

HEMA: 2-Hydroxyethyl methacrylate; from Sigma Aldrich.

IPDI: Isophorone diisocyanate (mixture of isomers); from Sigma Aldrich.

NaMAA: Sodium salt of methacrylic acid; from Sigma Aldrich.

MAOES: mono-2-(Methacryloyloxy)ethyl succinate; from Polysciences Inc.

MMA: Methyl methacrylate; from Sigma Aldrich.

PEGMA(#): Mono-methoxy poly(ethylene glycol) mono-methacrylate where # is the average degree of polymerisation of the PEG chain; from Polysciences Inc. or Laporte Performance Chemicals.

PPGMA(#): Mono-methoxy poly(propylene glycol) mono-methacrylate where # is the average degree of polymerisation of the PPG chain; from Laporte Performance Chemicals.

SSA: Styrene-4-sulfonic acid; from Sigma Aldrich.

TDI: Tolylene diisocyanate (mixture of isomers); from Sigma Aldrich.

Abamectin: insecticide, miticide, (10*E*,14*E*,16*E*,22*Z*)-(1*R*,4*S*,5'*S*,6*S*,6'*R*,8*R*,12*S*,13*S*,20*R*,21*R*,24*S*)-6'-[(*S*)-*alkyl*]-21,24-dihydroxy-5',11,13,22-tetramethyl-2-oxo-3,7,19-trioxatetracyclo[15.6.1.$1^{4,8}$.$0^{20,24}$]pentacosa-10,14,16,22-tetraene-6-spiro-2'-(5',6'-dihydro-2'*H*-pyran)-12-yl 2,6-dideoxy-4-*O*-(2,6-dideoxy-3-*O*-methyl-α-L-*arabino*-hexopyranosyl)-3-*O*-methyl-α-L-*arabino*-hexopyranoside, mixture of isomers *alkyl* = (*sec*-butyl:*iso*-propyl, 4:1).

Azoxystrobin: fungicide, Methyl (E)-2-2-6-(2cyanophenoxy)pyrimidin-4-yloxy-phenyl-3-methoxyacrylate

Chlorothalanil: Fungicide, Tetrachloroisophthalonitrile

Emamectin benzoate : insecticide, benzoate salt of (10*E*,14*E*,16*E*,22*Z*)-(1*R*,4*S*,5'*S*,6*S*,6'*R*,8*R*,12*S*,13*S*,20*R*,21*R*,24*S*)-6'-[(*S*)- *alkyl*]-21,24-dihydroxy-5',11,13,22-tetramethyl-2-oxo-3,7,19-trioxatetracyclo[15.6.1.$1^{4,8}$.$0^{20,24}$]pentacosa-10,14,16,22-tetraene-6-spiro-2'-(5',6'-dihydro-2'*H*-pyran)-12-yl 2,6-dideoxy-3-*O*-methyl-4-*O*-(2,4,6-

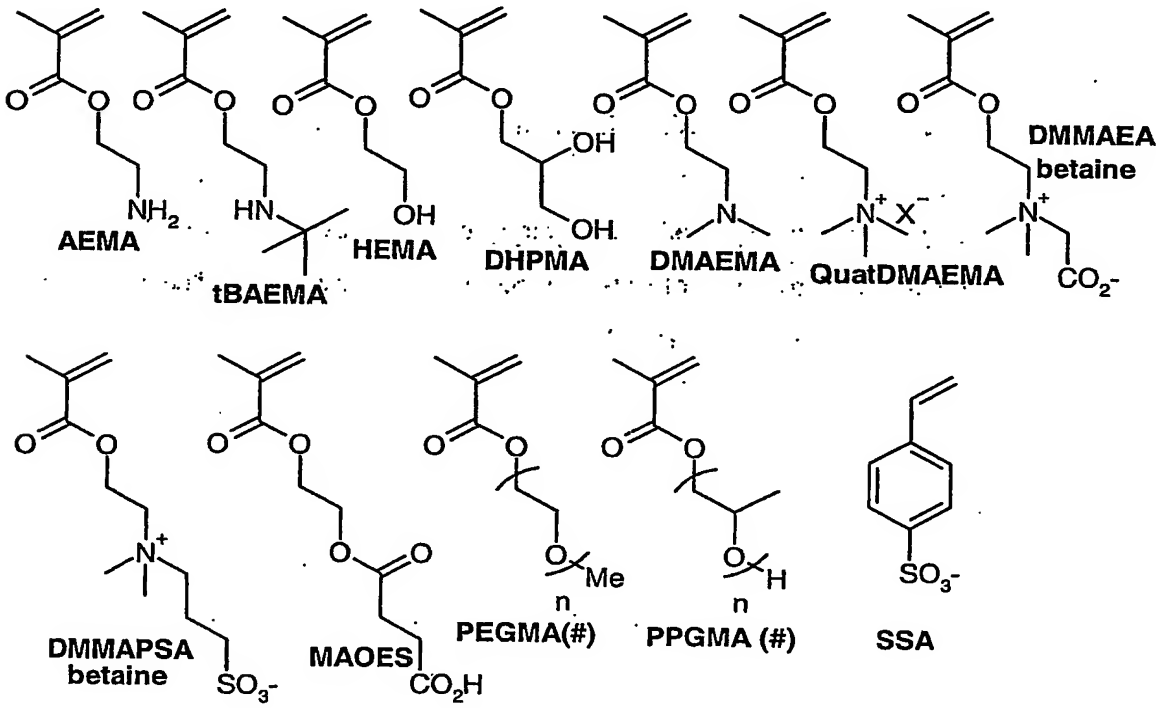
trideoxy-3-*O*-methyl-4-methylamino- α -L-*lyxo*-hexopyranosyl)- α -L-*arabino*-hexopyranoside, mixture of isomers *alkyl* = (*sec*-butyl:*iso*-propyl, 9:1).

Picoxystrobin: fungicide, methyl (*E*)-3-methoxy-2-[2-(6-trifluoromethyl-2-pyridyloxymethyl)phenyl]acrylate.

Thiamethoxam: insecticide, 3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4-ylidene(nitro)amine.

Avecia NeoResins, Waalwijk, Netherlands. Laporte Performance Chemicals, Hythe, UK. Polysciences Inc, Warrington, PA 18976, USA. Röhm GMBH, 64293 Darmstadt, Germany. Sigma Aldrich, Gillingham, UK.

For clarity the structures of the above monomers are given as:



GENERAL METHOD 1

This Example illustrates the synthesis of reactive polymeric surfactants by atom transfer radical polymerisation (ATRP).

General synthetic procedure:

In a typical polymerisation monomers at the required molar ratios were dissolved in a suitable solvent or solvent mixture (see Table 1). If the desired product was a non-ionic block or random graft copolymer then all the required monomers were used at once. If the

desired product was an ionic block copolymer then just the monomers for one block, either the hydrophilic or hydrophobic one, were used. The monomers for the second block were added in a second batch after the first batch reached high polymer conversion. Methanol-water mixtures (between 1:1 and 3:1 v/v) were most often used since many of the monomers were poorly soluble in organic solvents, e.g. AEMA.HCl, QuatDMAEMA, SSA, DMMAPSA betaine and DMMAEA betaine. Toluene was sometimes used if all the required monomers were soluble in aromatic hydrocarbons.

An appropriate initiator was added (see Table 1). For the preparation of non-ionic block co-polymers this was a polymeric macroinitiator such as a mono-2-bromoisobutyryl mono-methoxy poly(ethylene glycol), abbreviated PEG-Br (#) where # is the number of ethylene glycol units, prepared via the literature method (Jankova *et al.* Macromolecules, 1998, *31*, 538-541). For the preparation of graft copolymers or ionic block copolymers the initiator was a monomeric 2-bromoisobutyryl ester, which may be 4-(bromomethyl)benzoic acid (BMBA), ethyl-2-bromoisobutyrate (EtBiB) or a different monomeric 2-bromoisobutyryl ester (BiB-R). The amount of initiator added was dependant on the target molecular weight for the co-polymer and was calculated from the relationship:
(Moles monomer)/(Moles initiator) = Degree of polymerisation of copolymer
The target number average molecular weight, M_n, for each example is given in table 1 in units of Daltons, Da.

Also added was a ligand for *in-situ* formation of the copper complex (see Table 1). This was usually 2,2'-bipyridine (BPY) for polymerisations in methanol/water mixtures and N-n-propyl-2-pyridylmethanimine (PPMA), prepared via the literature method (Haddleton *et al.* Macromolecules, 1997, *30*, 2190-2193), for polymerisations in toluene.

The reaction solution was de-oxygenated by sparging with dry nitrogen gas for 15-30 min before being transferred to nitrogen filled vessel previously charged with the appropriate copper (I) salt to form the polymerisation mediating complex. This was normally copper (I) bromide, but copper (I) chloride was sometimes used (see Table 1). The reaction was carried out under nitrogen at a controlled temperature that ranged between 25 and 90 °C (see Table 1) for between 3 and 24 hours. The extent of the reaction was measured by ^{1}H-NMR spectroscopy. In the case of ionic block copolymers the second monomer or co-monomer mixture was added to form the second block when conversion of the first monomer batch exceeded 80%. On completion, the reaction solution was passed through a silica

column and the polymer isolated by evaporating the solvents under vacuum or by selective precipitation in hexane or diethyl ether. For a reaction requiring the post-polymerisation quaternisation of DMAEMA the reaction solution was diluted with toluene, cooled and filtered to remove insoluble material then the solvent was removed under vacuum. The polymer was dissolved in THF and 20% molar excess of iodomethane to tertiary amino groups added. The solution was stirred under nitrogen at 20 °C for between 16 and 20 hours and the polymer was isolated by selective precipitation into hexane. The polymer was then further purified by Soxhlet extraction with hexane for 24 hours followed by drying under vacuum at 50 °C.

The above general procedure was used to prepare the polymeric surfactants detailed in Table 1 where: -

Examples 1.1 to 1.3 illustrate carboxylic acid containing block and comb copolymers

Examples 1.4 to 1.6 illustrate amine and amine plus carboxylic containing block and comb copolymers

Examples 1.18 to 1.27 illustrate hydroxyl containing block and comb copolymers.

In the column showing the proportion of the monomers used, * indicates monomers added in a second batch to form the B block of a diblock copolymer.

Patent Example No	Structure	Monomers / mole %		Initiator	ligand	Copper salt	Solvent	Temp. / °C	Target M_n / Da
1.1	Non-ionic diblock	MMA **MAOES**	80 20	PEG-Br (45)	PPMA	CuCl	Toluene	90	6000
1.2	Non-ionic comb	MMA **MAOES** PEGMA(9)	75 10 15	EtBiB	PPMA	CuCl	Toluene	70	20000
1.3	Zwitterionic/ non-ionic comb	MMA **DMMAEA betaine** PEGMA(39)	58 32 10	BiB-R	BPY	CuBr	Methanol 75% Water 25%	20	16000
1.4	Anionic/ non-ionic comb	MMA **AEMA.HCl** **MAOES** PEGMA(23)	74.7 8.3 11.4 5.6	EtBiB	BPY	CuCl	Methanol 60% Water 40%	50	22000
1.5	Anionic/ non-ionic comb	MMA **AEMA.HCl** **MAOES** PEGMA(23)	65 13 12 10	EtBiB	BPY	CuBr	Methanol 65% Water 35%	50	20000
1.6	Anionic/ non-ionic comb	MMA **AEMA.HCl** **NaMAA** PEGMA(39)	60 24 6 10	BiB-R	BPY	CuBr	Methanol 75% Water 25%	20	16000
1.7	Non-ionic comb	MMA **AEMA.HCl** PEGMA (9)	71 10 19	EtBiB	BPY	CuBr	Methanol 65% Water 35%	50	20000
1.8	Non-ionic comb	MMA **AEMA.HCl** PEGMA(23)	84 5 11	EtBiB	BPY	CuBr	Methanol 65% Water 35%	50	20000
1.9	Cationic/ non-ionic comb	MMA **tBAEMA** QuatDMAEMA PEGMA(39)	55 20 15 10	EtBiB	BPY	CuBr	Methanol 65% Water 35%	50	20000

1.10	Cationic/ non-ionic comb	MMA AEMA.HCl QuatDMAEMA PEGMA(39)	60 24 6 10	BiB-R	BPY	CuBr	Methanol 75% Water 25%	20	16000
1.11	Non-ionic diblock	MMA AEMA.HCl	90 10	PEG-Br (45)	BPY	CuBr	Methanol 50% Water 50%	20	4000
1.12	Cationic/ non-ionic comb	MMA HEMA QuatDMAEMA (PP) PEGMA(23)	73.5 10 10 6.5	EtBiB	PPMA	CuCl	Toluene	70	20000
1.13	Cationic/ non-ionic comb	MMA HEMA QuatDMAEMA PEGMA(39)	60 24 6 10	BiB-R	BPY	CuBr	Methanol 75% Water 25%	20	16000
1.14	Zwitterionic/ non-ionic comb	MMA HEMA DMMAPSA betaine PEGMA(39)	60 24 6 10	BiB-R	BPY	CuBr	Methanol 75% Water 25%	20	16000
1.15	Anionic/ non-ionic comb	MMA HEMA SSA PEGMA(39)	60 24 6 10	BiB-R	BPY	CuBr	Methanol 75% Water 25%	20	16000
1.16	Anionic/ non-ionic comb	MMA HEMA SSA PEGMA(39)	60 24 6 10	BiB-R	BPY	CuBr	Methanol 75% Water 25%	20	32000
1.17	Anionic/ non-ionic comb	MMA HEMA NaMAA PEGMA(39)	60 24 6 10	BiB-R	BPY	CuBr	Methanol 75% Water 25%	20	16000
1.18	Non-ionic comb	PEGMA(39) PPGMA(7)	20 80*	PEG-Br (7)	BPY	CuBr	Methanol 75% Water 25%	20	21000

1.19	Non-ionic comb	PEGMA(39) **PPGMA**(7)	20 80*	PEG-Br (7)	BPY	CuBr	Methanol 75% Water 25%	20	11500
1.20	Non-ionic diblock, comb	PEGMA(39) **PPGMA**(7)	20 80*	PEG-Br (7)	BPY	CuBr	Methanol 75% Water 25%	20	11000
1.21	Cationic diblock	MMA **HEMA** QuatDMAEMA (PP)	45 5 50*	EtBiB	PPMA	CuCl	Toluene	90	7000
1.22	Cationic diblock	MMA **HEMA** QuatDMAEMA	30* 20* 50	BiB-R	BPY	CuBr	Methanol	20	10000
1.23	Non-ionic diblock	MMA **HEMA**	90 10	PEG-Br (45)	PPMA	CuBr	Toluene	90	4000
1.24	Non-ionic diblock	MMA **DHPMA**	50 50	PEG-Br (45)	BPY	CuBr	Methanol	20	7200
1.25	Non-ionic diblock	MMA **DHPMA**	37 63	PEG-Br (45)	BPY	CuBr	Methanol	20	6600
1.26	Non-ionic diblock	MMA **HEMA**	45 55	PEG-Br (45)	BPY	CuBr	Methanol	20	6600
1.27	Anionic diblock	MMA **HEMA** SSA	30* 20* 50	BMBA	BPY	CuBr	Methanol	20	10000

GENERAL METHOD 2

This Example illustrates the preparation of aqueous dispersions of milled agrochemicals in the presence of reactive polymeric surfactants

General Dispersion Procedure

The general procedure used to prepare dispersions should not be interpreted as a limitation on the invention.

Suspension concentrates (SC's) were prepared by milling the ingredients (Table 2) with number 4 zirconia beads in a Glenn Creston Spex 8000 shaker mill for 30 minutes. Typically, the SC consisted of 20% w/w solid agrochemical active ingredient in de-ionised water. The reactive polymeric stabiliser was used at concentrations of 0.5-10 w/w % with respect to solids (ratio by weight of polymeric stabiliser to suspended solid from 1: 200 to 1:10). The suspensions were assessed for particle size, the degree of foaming and the fluidity. The particle size was used as an indicator of the effectiveness of the polymeric stabiliser as a dispersant and milling aid. The quality of the dispersion of all dispersions in Table 2 was either "Excellent" or "Good" where "Excellent" describes generally a fluid SC with little or no foaming and a particle size of ≤ 2-3μm; and "Good" describes a fluid to slightly viscous SC with little to medium foaming and a particles size of ≤ 5μm.

The above general procedure was used to prepare dispersions detailed in Table 2 where the polymeric stabiliser used is indicated by its identifying number in Table 1. In Table 2, the column "% solids" indicates the % w/w solid agrochemical active ingredient in de-ionised water. The column "Polymer Concentration" indicates the % by weight of the stabilising polymer relative to the active ingredient. The size of the dispersed particles after milling is given in Table 2 in microns. N.m means not measured

Table 2

Dispersions Prepared using polymeric stabilisers prior to cross-linking

Dispersion Reference	Polymer (Table 1 Reference)	Cross-linking Group	Agrochemical	% solids	Polymer Concentration %	Size (μm)
2.1	1.1	CO2H	Picoxystrobin	20	5	1.61
2.2	1.1	CO2H	Abamectin	20	2	2.39
2.3	1.1	CO2H	Chlorothalonil	20	2	2.06

2.5	1.1	CO2H	Picoxystrobin	20	2	1.76
2.6	1.1	CO2H	Picoxystrobin	20	10	0.55
2.7	1.1	CO2H	Thiamethoxam	20	2	n.m.
2.8	1.2	CO2H	Picoxystrobin	20	5	1.52
2.9	1.2	CO2H	Azoxystrobin	20	2	1.48
2.10	1.2	CO2H	Chlorothalonil	20	2	2.16
2.12	1.2	CO2H	Picoxystrobin	20	2	1.61
2.13	1.2	CO2H	Picoxystrobin	20	10	0.77
2.14	1.2	CO2H	Thiamethoxam	20	2	n.m.
2.15	1.3	CO2H	Abamectin	20	2	1.44
2.16	1.3	CO2H	Azoxystrobin	20	2	0.95
2.17	1.3	CO2H	Chlorothalonil	20	2	1.78
2.19	1.3	CO2H	Thiamethoxam	20	2	n.m.
2.20	1.4	CO2H/NH2	Picoxystrobin	20	5	2.04
2.21	1.4	CO2H/NH2	Abamectin	20	2	1.32
2.22	1.4	CO2H/NH2	Thiamethoxam	20	2	n.m.
2.23	1.5	CO2H/NH2	Abamectin	20	2	2.4
2.24	1.5	CO2H/NH2	Abamectin	20	1	2.2
2.25	1.5	CO2H/NH2	Abamectin	20	0.5	3.4
2.26	1.5	CO2H/NH2	Azoxystrobin	20	2	1.4
2.27	1.5	CO2H/NH2	Azoxystrobin	20	1	1.0
2.28	1.5	CO2H/NH2	Azoxystrobin	20	0.5	1.8
2.29	1.5	CO2H/NH2	Chlorothalonil	20	2	2.0
2.30	1.5	CO2H/NH2	Chlorothalonil	20	2	2.8
2.31	1.5	CO2H/NH2	Chlorothalonil	20	1	2.1
2.32	1.5	CO2H/NH2	Chlorothalonil	20	0.5	3.2
2.36	1.5	CO2H/NH2	Emamectin	20	2	1.6
2.37	1.5	CO2H/NH2	Picoxystrobin	20	2	1.8
2.38	1.5	CO2H/NH2	Picoxystrobin	20	1	1.8
2.39	1.5	CO2H/NH2	Thiamethoxam	20	2	n.m.

2.40	1.5	CO2H/NH2	Chlorothalonil	20	2	2.4
2.41	1.8	NH2	Picoxystrobin	20	5	1.33
2.42	1.11	NH2	Picoxystrobin	20	5	1.08
2.43	1.6	NH2	Picoxystrobin	20	5	2.01
2.44	1.10	NH2	Picoxystrobin	20	5	1.54
2.45	1.7	NH2	Picoxystrobin	20	5	1.58
2.46	1.7	NH2	Abamectin	20	2	3.40
2.47	1.7	NH2	Azoxystrobin	20	2	1.93
2.48	1.7	NH2	Chlorothalonil	20	2	2.39
2.50	1.7	NH2	Picoxystrobin	20	2	1.72
2.51	1.7	NH2	Picoxystrobin	20	10	0.72
2.52	1.7	NH2	Thiamethoxam	20	2	n.m.
2.53	1.9	NH2	Abamectin	20	2	2.07
2.54	1.9	NH2	Azoxystrobin	20	2	1.21
2.55	1.9	NH2	Chlorothalonil	20	2	1.36
2.57	1.9	NH2	Thiamethoxam	20	2	n.m.
2.58	1.23	OH	Picoxystrobin	20	10	1.66
2.59	1.23	OH	Picoxystrobin	20	5	1.84
2.60	1.21	OH	Abamectin	20	2	1.62
2.61	1.21	OH	Chlorothalonil	20	2	2.33
2.63	1.21	OH	Picoxystrobin	20	5	1.55
2.64	1.21	OH	Picoxystrobin	20	2	1.73
2.65	1.21	OH	Picoxystrobin	20	10	0.5
2.66	1.21	OH	Thiamethoxam	20	2	n.m.
2.67	1.12	OH	Picoxystrobin	20	5	0.91
2.68	1.21b	OH	Abamectin	20	2	1.63
2.69	1.21b	OH	Azoxystrobin	20	2	1.06
2.70	1.21b	OH	Chlorothalonil	20	2	1.16
2.72	1.21b	OH	Thiamethoxam	20	2	n.m.
2.73	1.15	OH	Picoxystrobin	20	5	2.02

2.74	1.16	OH	Picoxystrobin	20	5	2.13
2.75	1.13	OH	Picoxystrobin	20	5	1.69
2.76	1.14	OH	Picoxystrobin	20	5	1.61
2.77	1.20	OH	Picoxystrobin	20	10	2.94
2.78	1.18	OH	Picoxystrobin	20	5	2.04
2.79	1.19	OH	Picoxystrobin	20	10	2.24
2.80	1.24	OH	Picoxystrobin	20	10	0.94
2.81	1.25	OH	Picoxystrobin	20	10	1.45
2.82	1.26	OH	Picoxystrobin	20	10	1.55
2.83	1.22	OH	Thiamethoxam	20	0.5	n.m.
2.84	1.27	OH	Abamectin	20	0.5	n.m.
2.85	1.27	OH	Thiamethoxam	20	2	n.m.
2.86	1.27	OH	Thiamethoxam	20	0.5	n.m.

EXAMPLES 3.1 TO 3.27

These Examples illustrate the cross linking of the polymeric stabiliser by reaction with a cross-linking substance to form a particulate suspension according to the present invention. The following procedure was used: -

Hydroxy and amine functional polymeric stabilisers were cross-linked by either (i) dispersing TDI in the aqueous phase of the SC, allowing some time for the TDI to adsorb on to the particles, then heating at 50°C for 1h min or stirring at room temperature for 3 hours, or (ii) dispersing IPDI in the aqueous phase of the SC, allowing some time for the IPDI to adsorb on to the particles, then adding diethylene triamine (DETA) to react with excess isocyanate.

Carboxylic acid functional RPS SC's were cross-linked by dispersing CX-100 or CX-300 into the SC at pH ≥9 and stirring at room temperature for 30 minutes to achieve adsorption of the cross-linker. The pH was reduced to ~2 and, after stirring for a further 1 hour, a small amount of EDTA was added to react with excess carbodiimide.

The above general procedures were used to prepare the dispersions detailed in Table 3. The quality of all suspension concentrates of the invention illustrated in Table 3 was deemed either "excellent" or "good" where "excellent" describes a sample in which

there was no material change in particle size or viscosity of the SC during the cross-linking reaction and "good" indicates that a small degree of aggregation was encountered during the cross-linking reaction, but that there was no major change to the suspension properties. In Table 3, the dispersion being cross-linked is indicated by its reference number in Table 2 which in turn identifies the polymeric surfactant by its reference number in Table 1.

Table 3

Cross-Linked Suspension Concentrates According to the Invention

Example	Dispersion Reference	Polymer (Table 1 Reference)	**Cross-Linking Substance**	**Size (μm)**
3.1	2.1	1.1	CX-300	1.04
3.2	2.8	1.2	CX-300	1.10
3.3	2.20	1.4	CX-300	2.04
3.4	2.21	1.4	CX-100	Not measured
3.5	2.21	1.4	CX-300	Not measured
3.6	2.41	1.8	TDI	3.08
3.7	2.41	1.8	IPDI	1.08
3.8	2.42	1.11	TDI	4.58
3.9	2.42	1.11	IPDI	1.01
3.10	2.45	1.7	TDI	3.79
3.11	2.45	1.7	IPDI	1.31
3.12	2.43	1.6	TDI	1.50
3.13	2.43	1.6	IPDI	1.40
3.14	2.43	1.6	CX-300	1.25
3.15	2.44	1.10	TDI	1.17
3.16	2.44	1.10	IPDI	1.09
3.17	2.59	1.23	TDI	3.51
3.18	2.59	1.23	IPDI	1.18
3.19	2.63	1.21	TDI	1.95

3.20	2.63	1.21	IPDI	1.79
3.21	2.67	1.12	TDI	1.00
3.22	2.67	1.12	IPDI	1.03
3.23	2.73	1.15	TDI	1.90
3.24	2.73	1.15	IPDI	1.84
3.25	2.76	1.14	TDI	1.84
3.26	2.76	1.14	IPDI	1.32
3.27	2.78	1.18	IPDI	1.40

CLAIMS

1. A particulate suspension comprising a liquid phase having suspended therein a solid substantially insoluble in said liquid phase wherein the suspension is stabilised by the reaction product of

(i) a polymeric stabiliser having a hydrophilic moiety and a hydrophobic moiety and comprising a plurality of vinylic monomers, not being exclusively of vinylic esters or of their hydrolysed products, at least some of which contain functional groups capable of undergoing cross-linking nucleophilic or condensation reactions and

(ii) one or more substances contained in the liquid phase capable of undergoing a cross-linking reaction with said functional groups

wherein the ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended solid is less than 1 part of polymeric stabiliser per 5 parts of suspended solid.

2. A process for the manufacture of a suspension of a particulate solid in a liquid medium which comprises the steps of

(i) milling the solid in the presence of the liquid medium and a polymeric stabiliser having a hydrophilic moiety and a hydrophobic moiety and comprising a plurality of vinylic monomers, not being exclusively of vinylic esters or of their hydrolysed products, at least some of which contain functional groups capable of undergoing cross-linking nucleophilic or condensation reactions; and subsequently

(ii) reacting said polymeric stabiliser with one or more substances contained in the liquid phase and capable of undergoing a cross-linking reaction with said functional groups

wherein the ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended solid is no more than 1 part of polymeric stabiliser per 5 parts of suspended solid.

ABSTRACT

A particulate suspension comprises a liquid phase having suspended therein a solid, for example an agrochemical, substantially insoluble in the liquid phase wherein the suspension is stabilised by the reaction product of (i) a polymeric stabiliser having a hydrophilic moiety and a hydrophobic moiety and containing functional groups capable of undergoing cross-linking reactions and (ii) one or more substances contained in the liquid phase capable of undergoing a cross-linking reaction with said functional groups, wherein the ratio by weight of (a) the polymeric stabiliser prior to cross-linking to (b) the suspended solid is less than 1 part of polymeric stabiliser per 5 parts of suspended solid.